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RECENTLY PUBLISHED RESEARCH OF THE MOSCOW CRDER OF LENIN STATE UNIVERSITY DARKI M. V. LONDBOROV

\*Determination of Active Hydrogen With the Grignard Reagent in an Atmosphere of Carbon Dioxide: II, A. P. Terent'yov, K. D. Shcherbakova, Lab Org Chem imeni N. D. Zelinskiy, Moscow Order of Lenin State U imeni M. V. Lomonosov

"Zhur Obshch Khimii" Vol 15, 1945, pp 86-9

Various alcohols, glycols, phenols, acids, and amino derivatives were analyzed by the method previously described. The method yielded good results with all the above-mentioned compounds, except tertiary alcohols and compounds inscluble in ether. The former gave higher results, presumably because water was split off in the presence of MeMgI. The latter do not react with MeMgI because of their insolubility in Et20.

"Vapor Pressure of Binary Systems: I," K. A. Dulitsknya, Lab Chem Thermodynamics, Moscow Order of Lenin State U imeni M. V. Lomonesov

"Zhur Obshoh Khimii" Vol 15, 1545, pp 9-21

Total and partial wapor pressures were measured on modified Vreveky apparatus for the systems: (1) glycerol-water at 25, 50, and 75°, (2) glycerol-Meckl at 25, 50, and 62.5°, (3) glycerol-EtoE at 25, 50, and 75°, (4) MeOH-water at 25, 50 and 62.5°, and (5) EtOH-water at 500. Caly positive deviations from Rapult's law were observed for any system except system

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(1), which and a negative deviation for all concentrations. The relation between total vapor pressure of binary systems and temperature follows the Heiglein equation. The relation of the partial pressure of the components of the system and the composition of the system follows those of the Bancroft equation.

"Isomerization of the Dimethyl Ether of 1,4-Dihydro-CL-Naphthohydroquinone," A. P. Terent'yev, P. P. Shavolova, Lab Org Chem, Moscow Order of Lenin State U imeni M. V. Lomonesev

"Zhur Obshch Khimii" Vol 15, 1945, pp 142-5

It was shown that the di-Me ether of 1,4-dihydrook -naphthohydroquinone (5, 8 -dihydro - 1,4-naphthalenediol) when heated with NaCMe isomerizes into the corresponding 1,2-dihydro derivative. The initial 1,4-djhydro- CX -naphthoquinone was prepared by condensation of butadiene with quinone and the product treated with HBr in AcOH gave 5,8-dihydrory-1,4-dihydro-naphthalene, m. 2120, which, treated with Me\_SO<sub>h</sub> in 20% NaOH, gave the di-Me ether (I) of 1,4-dihydro-x -naphthalydroqu' none m 500, 298-3000. The ether heated with 10% MeONa in MeOH to 1300 for 6 hours in a sealed tube isomerized quantitatively into the d1-Me ether (II) of 1,2 dihydru- & -naphthohydroquinone, m 540. I yields a crystalline dibromide (2,5-dibrozo-1,2,3,4tetrahydro-5,8-dimethoxynaphthalene), m 1240; II fails to yield a stable dibromide. Heating of either ether with S at 2500 yielded the mono-Me other of naphthohydroquinone, m 84-50. II shows an MR exaltation of 2.34; I has a normal MR. Reduction of II in keOH by means of Na gave the Me ether of tetrakydronaphthohydroquinone, m 39-400; I failed to reduce under these conditions. II copolymerizes readily with butadiene (Na catalyst); I does so very slowly.

"The Chemical Nature of Volution," A. N. Belozerskiy, Lab Plant Biochem, Moscow Order of Lenia State U imeni M. V. Lomonssov

"Mikrobiologiya" Vol 14, No 1, 1945, pp 29-34

A protein-free substance was extracted from 2-4-day cultures of Spirillum volutans, in amounts of 8-12% of dry weight, which proved to be a mholeic acid of the yeast type. It was named "volution-nucleic acid" (I). Six-day cultures did not contain I. A 0.2% solution of Na<sub>2</sub>CO<sub>3</sub> was used for extraction of the bacterial mass. Since rapid neutralization occurred, a 10% soda solution was added drop-by-drop until a stable alkaline reaction was reached. Acidification with AcOH precipitated nucleoproteins and treatment of the filtrate with alcohol and HCl yielded I. Hydrolysis of I gave all the purine and pyrimidine bases characteristic for yeast-nucleic acid (II). Analysis of I gave:



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total N 9, P 10, S 0. 9, and pentoses 24% of dry weight. Thus, I contains considerably more P than II, and it is a high-molecular weight E2SO4 ester. Volutin (metachromatin) (III) is a stored product and not a component of nucleus or cytoplasm, since the cell maintains its activity in the absence of III.

"Antithyroid Activity of 4-Mathyl-2-Thiouracil,"
Ya. M. Kabak, A. A. Beer, A. E. Rabkina, Moscow
Order of Lenin State U imeni M. V. Lomonosov

"Byul Ers Biol 1 Med" Vol 21, 1946, pp 37-40

No mortalities were observed when 4-methyl-s-thicuracil was administered to rats in dosage under 60 mg -per day. The effects of prolonged treatment included slowing of growth and of heart action. Characteristic thyroidectomy cells became evident. Implantation of the gland, after such treatment, into tadpoles failed to induce metamorphosis in the latter.

"Kinetic Analysis of the Eistherment ingon?" Methane to Acetylene and Hydrogen, " S. S. Varilyev, Moscow Order of Lenin State U imeni M. V. Lomonosov

"Zhur Fiz Khimii" Vol 20, 1946, pp 517-38

Literature data on transformation of CH<sub>k</sub> into C<sub>2</sub>H<sub>2</sub> and H<sub>2</sub> in an electrical discharge are collected and supplemented by some unpublished observations. A theory of the process is derived. It is based partly on the mass law, and partly on some empirical rules. It gives the connection between the yield of C<sub>2</sub>H<sub>2</sub> and the electric properties of the discharge, the dimensions of the reaction vessel, the rate of gas flow, and the gas composition. Dbserves an agreement between experiment and theory.

"An Antomatic Apparatus for the Production of Distilled Water," P. P. Pugachevich, Moscow Order of Lenin State U imeni M. V. Lomonosov, Sci Res Inst. of Phys

"Zavod Lab" Vol 12, 1946, pp 762

No details given.

"The Hormal Tungstates of Bubidium and of Cesium,"
V. I. Spitsyn, Moscow Order of Leniu State U imeni
M. V. Lemonosov

"Zhur Gbahch Khimii," Vol 17, 1947, pp 11-22

Attempts to prepare the simple tungstates by fusion of 405 with the alkali metal carbonates failed to give pure products, owing to thermal dissociation and volatility. Synthesis by way of a





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double exchange of the sulfates or carbonates with BeWO<sub>1</sub> also was unsuccessful, owing to reversibility of the reaction. Most successful was the double exchange of the chlorides with AgwO<sub>1</sub> (prepared by precipitation of AgwO<sub>2</sub> with NaWO<sub>1</sub> and drying the washed precipitate at 100-110°), preferably w fusion at 400-500° with a 20-25% excess of AgwQ<sub>2</sub>. The product is kept in the dark over P<sub>2</sub>O<sub>5</sub> and alkali, crushed rapidly and twice leached with water (each time 50 ml per 5 g initial chloride) under exclusion of CO<sub>2</sub>; the first leaching is done in the cold, 10-12 hours; the second at boiling 10-15 minutes. The yield is 90-92% of the theory, the losses occurring by absorption of part of the solution by the AgCl precipitate.

Analysis confirmed the simple formulas Nb<sub>2</sub>WO<sub>4</sub> and Cs<sub>2</sub>WO<sub>6</sub>.

"Determination of Active Hydrogen by Grignard Reagents in a Carbon Dioxide Atmosphere, IV," A. P. Terent'yev, K. D. Shcherbakova, N. V. Kremenskaya, Moscow Order of Lenin State U imeni M. V. Lomondow

"Zhur Obshch Khimii" Vol 17, 1947, pp 100-4

The use of MeMgBr and MeMgCl, in place of the usual MeMgI, in the active H determination in CO<sub>2</sub> atmosphere as described previously was investigated. MeMgBr 's suitable on the basis of trials with the following substances: BnOH, borneol, pyrocatechol, MeEtC(OH)Ph, Ph<sub>2</sub>C(OH)Et, PhCH(OH)Et, BzCH, o-AcCCGRCO\_H, mandelic acid, citraconic acid, PhRH<sub>2</sub>, p-McCH<sub>2</sub>MH<sub>2</sub>, 1-(1-piperidyl)-3-aminopropane, RCCHHPh, and 2-acetylpyrrole. The deviations noted were: EtPhCHOH gave 1.11 and EtPh<sub>2</sub>COH 1.25 H atoms, evidently because of the dehydrating action of the reagent. Primary amines gave figures slightly lower than theoretical (PhRH<sub>2</sub> 1.94, 1-(1-pipe:idyl)-3-aminopropane. 1.8 H) due to interaction of CO<sub>2</sub> with the primary reaction product, so that the second stage does not go quite to completion for the less soluble browides, while the soluble icdides are able to go to completion. MeMgCl gave consistently good results with: 1- and 2-naphthols, salicylic acid, borneol, and p-nitrophenol. Mydroquinone, because of poor solubility, gave low results (1.56-1.63). 2-C<sub>1</sub>OH,NH<sub>2</sub>Gave 0.99 H at Et<sub>2</sub>O reflux, and 1.98 H at 1000 Behzidine gave 2.0 H at low and high (1000) temperatures. AcCH<sub>2</sub>CO<sub>2</sub>Et gave 1.01 H. When the reaction was run in CH<sub>2</sub>, thysol gave 1.03 H, salicylic acid 2.0, and Ph<sub>2</sub>HH 1.0 H. Generally, MeMgCl was less active than the Br compound and tended to lose its titer more rapidly than the latter on standing.

"Syntheses With Acrylonitrile: IV, Reduction of Mitriles With Sodium in Alcohol Medium," A. H. Most, A. P. Terent'yev, Moscow Order of Lenin State U imeni M. V. Lamonomev

"Zhur Obshch Khimii" Vol 17, 1947, pp 105-8



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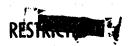
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In unpublished work of Longinov and Filippov, 1935, it was found that when the Na used for the reduction of esters contains even as little as 0.01% of K the yields of the alcohols drop rapidly. In the reduction of BuCh(CO2Bt)2 the yield is zero when the Na contains 0.01% K. However, if the amount of K is increased, the yields rise again and become normal with 2% K. This is important since Na is usually contaminated with traces of K. This study was extended to the reduction of EtaNCH2CH2CH and 1-piperidinepropionitrile in Buoff by the Suter and Moffet method. Technical Ma gave 38-50% of the diamine, pure Na 51-63%, while technical Ma with the addition of 2% K gave 65.9-70% diamine, in the case of KtmCNgCRgCN. With the piperidyl compound the yields were 42-46%, 48.9-57.2%, and 48-57%, respectively, thus indicating a similarity to the results obtained in ester reduction. The high-K Ma gave reproducible yields and tended to give smaller amounts of higher-boiling products (pre-sumably secondary smines). The Rupe technique (immediate steam distillation) gave similar results, but was inconvenient due to the low volatility of the products.

"Catalytic Transformations of Heterocyclic Compounds: IXI. Transformation of Furan and Furanidine Into Hydrocarbons," Yu. K. Yur'yev, V. A. Tronova, M. Ya. Kusnetsova, E. C. Hovosadova, Moscow Order of Lenin State U imeni N. V. Losmosov

"Zhur Obshoh Khimii" Vol 17, 1947, pp 131-6

Furanidine (5-6 g) was passed over Al<sub>2</sub>O<sub>5</sub> in a strong current of C<sub>2</sub>H<sub>2</sub> at 375°; the catalyst slowly became covered with a brown deposit and had to be regeneral ated conscionally by air-blowing. The catalyst temperature rose initially up to 405-450°, becoming stabilized generally at about 365°. The yield of products was 1.5-1.95 g. The combined products from 10 runs were dried over CaCl<sub>2</sub> and fractionated. A fraction (0.75g), b 78-84°, 75 1.4701, contained cyclohexadiene, formed evidently by bond redistribution of the initially formed cyclohexyne. A fraction (1.1 g), by 100-20°, 75 1.474°, appeared to be a product of C<sub>2</sub>H<sub>2</sub> condensation over Al<sub>2</sub>O<sub>5</sub>, admixed with methyloyolchexadiene (from propylene and C<sub>2</sub>H<sub>2</sub>). Furan (5 g) was passed over activated C in 1.25 hours in a H stream at 375-500°; the best yield (16\$) of butadiene was used at 200-450°, the bost yield of butadiene (20.1\$) was obtained at 425° when 5 g furan was passed through the catalyst in 1.6 hours. Results are interpreted as favoring the possibility of petroleum formation from carbohydrate matter in nature.





"Surface Tension of Solutions of Molten Salts, II," V. K. Semenchenko, L. P. Shikhobalova, Moscow Order of Lenin State U imeni M. V. Lomonosov.

"Zhur Fiz Khimi1" Vol 21, 1947, pp 707-14

Surface tension of five binary melts was determined by the method of the maximum bubble pressure. The or of unmixed salts at 9000 and 1,1000; respectively are: Id2SO4 224 and 211 dynes/om, MaCl 109 and 95, EC1 91 and 75, RbCl 83 and 66, CaC1 72 and 59 (at 1,050°), and BeSO<sub>4</sub> 175 (1,000°) and 172 (1,050°). K2804 at 1,0750 has o- = 144.3. The error is = 1 dyne/cm. The o of Li2SO4 is lowered by the above chlorides, more so the smaller the co of the chloride. At about 1-5 molecular \$ of the chloride or is independent of its concentration; otherwise, the curve of commands and fraction is regular and slightly donver toward the origin of the coordinates. The curve for Li280h + BaCl2 has a minimum (163 at 1,0000) at the equimolecular composition. For all melts, the curve of comparish temperature is slightly compave toward the origin of the coordinates. The value of o is determined by the "generalized moment" of the ion, i.e., its charge divided by its crystallographic radius. The greater the difference between the "generalized moments" of the ions of solvent and solute, the greater the surface activity.

"Relation Between the Viscosity of Liquids and Their Pressure," G. M. Panchenkov, Moscow Order of Lenin State U imeni M. V. Lomonosov

"CR Acad Sci URSS" Vol 51, 1946, pp 365-8

The following relation between viscosity and temperature for liquids had previously been developed:

7=5N6R JW2/No (P40/M5/6) JT @E/RT(1-6-6/RT)2

when his the viscosity coefficient, R the gas constant,  $R_0$  the Avogadro number,  $\omega$  the actual molecular volume,  $\rho$  the density of the liquid, at the molecular weight, T the abstract temperature, and  $\theta$  the bond energy of the molecules. Since both  $\theta$  and  $\rho$  are functions of pressure, the above formula indicated a means to calculate  $\eta$  as a function of pressure. Calculated values of  $\eta$  for ExM and Ethr indicated fair agreement with experimental data over a range from 1 to 12,000 atmospheres.

"Appearance of Free Atomic Hydrogon on the Marquiny Cathode and the Mechanism of the Cathodic Reduction of Tungstate," V. S. Bagotskiy, Z. A. Iofa, Moscow Order of Lenin State U imeni M. V. Lomonosov

"CR Acad Soi URSS" Vol 53, 1946, pp 439-42







aggravation, and for the fact that in certain atoms and atomic ensembles (inorganic catalysts) this property is practically absent.

"Surface Reactions. III. Reaction Between Solutions of Hydrolyzod Salts and Ash-Free Active Carbons,"
L. Lepin, G. Strakhova Moscow Order of Lenin State U imeni M. V. Lomongesy

"Acta Physicochimica URSS" Vol 21, 1946, pp 1089-1104
"Zhur Fiz Khimii" Vol 20, 1946, pp 743-52

Adsorption of Cl from solutions of AlCl<sub>2</sub>, CuCl<sub>2</sub>, FeCl<sub>2</sub>, and PbCl<sub>2</sub> by ash-free carbon is greater than from solutions of KCl or BaCl<sub>2</sub>. Addition of HCl increases the adsorption of Cl from KCl, BaCl<sub>2</sub>, or AlCl<sub>2</sub> solutions because H ± neutralizes the OH ions leaving the carbon. Addition of HCl lowers the adsorption of Cl from CuCl<sub>2</sub>, FeCl<sub>2</sub>, and PbCl<sub>2</sub> solutions because of the formation of CuCl<sub>2</sub> and FbCl<sub>2</sub> solutions because of the formation of CuCl<sub>2</sub>, FeCl<sub>2</sub>, and FbCl<sub>2</sub> carbon gives rise to precipitates.

"Sulfonation of Furan Derivatives," A. P. Terent'yev, L. A. Kazitsyna, Mossew Order of Lenin Stete U imeni M. V. Lomonserv

"CR Acad Sci URSS" Vol 55, 1947, pp 625-8

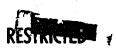
Silvan (I), 2,5-dimethylfuran (II), commarone (III), and thiophene (IV) were sulfonated with C<sub>5</sub>H<sub>5</sub>N-8O<sub>5</sub> in 1:3 molar ration at 100-10° 8-10 hours in a sealed tube. I gave 80% 2-methyl-3,5-furandisulfonic acid (V), isolated as the Ba and Na salts. Pure V was not obtained since it is very hygrosoptic. II gave 2,5-dimethyl-3-furansulfonic acid as the Ba salt. III gave in quantitative yield 2-commaronesulfonic acid, isolated as the Ba and Ag salts. IV gav. a disulforic acid, the constitution of which has not yet been established. C6H6, MePh, and 1,3,5-Me<sub>3</sub>C<sub>6</sub>H<sub>3</sub> were not sulfonated by C<sub>5</sub>H<sub>5</sub>N-SO<sub>3</sub> whereas PhOMe gave a quantitative yield of a monosulfonic acid.

"Sulfonation of Indole and Its Homologs," A. P. Terent; yev, L. V. Tsymbal, Moscow Order of Lenin State U imeni M. V. Lomonegov

"CR Anad Sci URSS" Vol 55, 1947, pp 833-5

The Ba salt of 1-indolesulfcaic acid (I) was prepared by sharing a finely divided aqueous suspension of 1 g indole (II) with 8 g Ba(CE)<sub>2</sub> and 4 g C<sub>5</sub>H<sub>5</sub>N-SC<sub>5</sub> in an ice bath 1.5 hours. The excess Ba(OH)<sub>2</sub> was precipitated with CO<sub>2</sub> and removed by filtration. The filtrate was concentrated to a small volume in the constant presence of NH<sub>5</sub> and 1 g. I was precipitated with excess BtOH. Its constitution was proven by analysis and the hydrolysis of I to II. The yield of the Ba salt of 2-indolesulfonic acid was improved to practically quantitative by sulfonation of II with a 2- or 3-molar excess of C<sub>5</sub>H<sub>5</sub>N-SO<sub>3</sub> at 120-40° (scaled tube).







The electron conductivity of WO<sub>3</sub> is considered as the mechanism for the cathodic reduction of the yellow anhydride WO<sub>3</sub> to the blue W<sub>O</sub>O<sub>5</sub> in electrolytic solutions. The theory that free atomic H in solution near the cathode acts as an intermediate agent in the reduction process is excluded. Simple experiments are described which support the electron conductivity theory and are explained without any assumption as to the appearance of free H in solutions near the cathode

"Active Charcoals and Adsorption From Solutions,"
O. M. Dzhigit, M. M. Dubinin, A. V. Kiselev, K. D.
Shcherbakova, Moseow Order of Lenin State U imeni M. V.
Lomonosov

"CR Acad Sci URSS" Vol 54, 1946, pp 141-4

The adsorption of mainly butyl and heptyl alcohols from water solutions by means of six different charcoals ranging widely in pore size was investigated to show the effect of the pore structure on the limit adsorption of alcohols of limited solubility in water. The charcoal structure was shown to have a strong effect on the shape of the adsorption isotherms and on the values of limit adsorption. The rule of constant adsorbed limit volumes was approximately trus for each of the carbons studied for the four alcohols butyl to heptyl. The micropores of the charcoals are equally accessible to the different alcohols and are densely filled by the alcohol molecules at limit adsorption.

"The Ensemble and Aggravation Principles in Catalysis: II. The Aggravation Principle and Structural Classification of Catalysts," N. I. Kobozev, Moscow Order of Lenin State U imeni M. V. Lomonsav

"Acta Physicochimica "RSS" Vol 21, 1946, pp 943-57

Catalysts are classified as to degree of complexity of the structure of active center. The smallest cluster of atoms still possessing catalytic properties is termed the "active element" and is denoted of frequently coincides with some chemical element. Two principal types exist involving aggravation of 2 and its association. Aggravation of active element-formation of active aggravate. This involves attachment of any molecular groups that are catalytically nonspecific, thus increasing the molecular weight of the catalyst, molecular potential, number of degrees freedom, number of bonds, and total energy. Examples given. A structoral classification of catalysts, covering all known types of active structures, is developed. The carriers are considered not only as fixation agents but also as aggravators of active elements (agons, protogons). This conception underlies the treatment of enzymes as highly aggravated structures, settling many contradictions in Willstatter's scheme. An explanation is suggested for the particular propensity of ions and large molecules to adsorptional





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Its constitution was proven by showing that sulfonation taxes place in skatole but not in 2-methylindole. The preparation of C5H5H-SO3 is described.

- E N D -

P. Carlotte

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